Effect of Oxidation State of Iron Ions on the Viscosity of Silicate Melts

Sohei SUKENAGA[1), 2)*], Takeshi OHSUGI[3)], Yosuke INATOMI[1)], Yoshiaki GONDA[1)], Takashi WATANABE[4)], Noritaka SAITO[1)] and Kunihiko NAKASHIMA[1)]

1) Department of Materials Science and Engineering, Kyushu University, 8190395, Japan

2) CEMHTI CNRS, Orléans 45071, France

3) Department of Decommissioning and Waste Management Nuclear Science Research Institute, Tokai Research and Development Center, Japan Atomic Energy Agency, 3191195, Japan

4) Department of Chemistry and Materials Science, Tokyo Institute of Technology, 1528550, Japan

Abstract: Viscosity of R_2O-SiO_2-Fe_xO (R=Li, Na or K) melts was measured by a rotating cylinder type viscometer with a gas-tight furnace. The measurements were carried out as a function of systematically changing oxygen partial pressure controlled by Ar-based gases at 1773 K. In addition, the samples were molten under each of the atmospheres at 1773 K for 4.5 h and then quenched on a cupper plate. These quenched vitreous samples were chemically analyzed for quantifying oxidation state of iron ions. The ratio of Fe^{2+} to Fe^{3+} in the glasses decreased with increasing the oxygen partial pressure in all the samples. In parallel, the viscosity of the melts decreased with increasing the ratio of Fe^{2+} to Fe^{3+}. The data indicates that the increase of Fe^{2+} ion that behaves as a network modifier, would result in depolymerisation of the silicate anions. It should be also noted that the viscosity of the melts was decreased in the order of alkali cationic radius (K > Na > Li) when the ratio of Fe^{2+} to Fe^{3+} in the melts was comparable; it would be due to the change in the coordination structure of Fe^{3+} in these melts.

Key words: viscosity; silicate melts; iron oxides; oxygen partial pressure

1. Introduction

Iron oxide containing silicate melts are important molten materials in some of the industrial processes at elevated temperature, such as glass making and pyrometallurgical extraction (as slags). In pyrometallurgical process, viscosity of slag is an important physical property to estimate the fluidity of the molten slags. Since the viscosity of melts is one of structure sensitive properties, viscosity is also important to understand the microstructure of molten slags. It is well known that the oxidation state of iron ions (Fe^{2+} and Fe^{3+}) in silicate melts changes dependent on the condition of the processes that the slags are employed [1-15]. In addition, FeO (Fe^{2+}) is known to behave as a network modifier, while Fe_2O_3 (Fe^{3+}) is an amphoteric oxide like Al_2O_3. Therefore, the ratio of Fe^{3+} to Fe^{2+} (Fe^{3+}/Fe^{2+}) in the melts would strongly affect the viscosity. The viscosity data of the iron oxide containing slags with the variation of Fe^{3+}/Fe^{2+} should be important for optimization of practical operation for high-temperature metallurgical processes. However, the relationship between the viscosity and the oxidation state of iron ion has not been well understood.

In the present paper, iron oxide containing alkali silicate system was selected for a fundamental study of iron oxide containing slags. The effect of oxygen partial pressure on the viscosity of the melts was examined by using rotating cylinder method. Ar-based gases, which were known to be less soluble to silicate melts than CO_2 based gas [16,17], were employed for controlling the oxygen partial pressure when we examine the effect of Fe^{3+}/Fe^{2+}

on the viscosity. Viscosity changes with the oxidation state of iron ions and the kind of alkali oxides were mainly explored.

2. Experimental

2.1 Sample preparation

Table 1 shows the initial compositions of the samples for the viscosity measurements. The samples were prepared from reagent grade SiO_2, Fe_2O_3, Li_2CO_3, Na_2CO_3 and K_2CO_3 powders (suppliers: Sigma Aldrich, Inc.). These reagents were precisely weighed to form given compositions and mixed in a mulite mortar thoroughly. The mixtures were placed in a Pt crucible and then melted at 1773 K in a resistance furnace for 30 minutes under air. Finally, the melts were quenched on a cupper plate. Then these quenched samples were clashed into powders and these powders were employed for viscosity measurements.

Table 1 Initial compositions (mol%) of the samples for viscosity measurements.

Sample	SiO_2	Fe_2O_3	Li_2O	Na_2O	K_2O
LSF	60	10	30	-	-
NSF	60	10	-	30	-
KSF	60	10	-	-	30

2.2. Measurement

2.2.1. Apparatus

The viscosities of the samples were measured by rotating cylinder method [18,19] in the present study. **Figure 1 (a)** represents the schematic illustrations of an inner cylinder rotating viscometer with a gas tight furnace, which can allow us to do the measurements under well-defined oxygen partial pressure. An electric resistance furnace with six U-shape $MoSi_2$ heating elements was employed for heating. An acrylic box, which was mounted on the top of the furnace as shown in Fig.1-(a), was used to isolate the system from the outside atmosphere during the measurements. The dimensions of a crucible and a bob are illustrated in Fig.1-(b). The crucible and bob, both of Pt-20mass%Rh, were employed in the experiments. The acquisition of the relative torque exerted on the inner cylinder (bob) was carried out by using a commercial viscometer. An apparent viscosity of the sample was calculated based on the reference relationship between the viscosity and the relative torque value, which was obtained using several kinds of silicone oil (viscosity range: 0.10~1.0 Pa·s) beforehand. Then after that, the measured apparent viscosity were corrected for the thermal expansion of the crucible and the bob by the following equation:

$$\eta = \frac{\eta'}{(1+\alpha T)^3}...(1)$$

where η, η' and α and T are a viscosity, an apparent viscosity, a thermal expansion coefficient and an absolute temperature, respectively.

The calibration of the viscometer at high temperature were made by using standard reference materials for high temperature viscosity measurements (SRM2 type slags) [20].
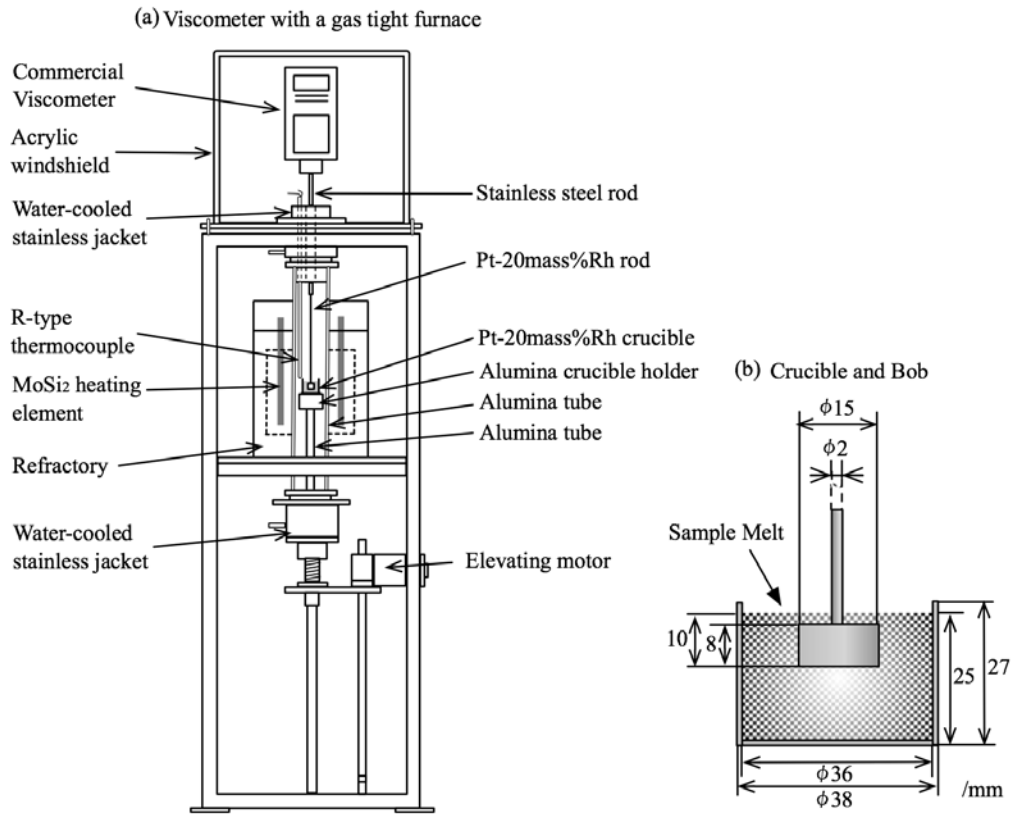
Fig.1 Schematic illustrations of (a) the apparatus for viscosity measurements and (b) the dimensions of a crucible and a bob.

2.2.2. Procedure

It is general that oxygen partial pressure of the atmosphere is controlled by using CO-CO_2 gas mixtures. On the other hand, Sumita *et al.*[16] examined the effect of CO_2 content on the viscosity of calcium ferrite slags, they reported that CO_2 gas easily solved into the melts and viscosity increased with the content of CO_2 in the melts. Since Ar-based gases are known to be slightly soluble to oxide melts [17], we employed some of the Ar based gases to control the oxygen partial pressures. The atmospheres employed in the present study are listed in **Table 2** with the oxygen partial pressures of these gases; the values of the oxygen partial pressures were examined by using a ZrO_2-CaO oxygen probe. We measure the viscosity under continuously varying oxygen partial pressures by changing the atmospheres in the sequence of Air, Ar-1%O_2, Ar, high Purity Ar, and Ar-1%H_2.

Table 2 Oxygen partial pressure of the atmospheres employed for the viscosity measurements. The oxygen partial pressures of the Ar-based gases were determined by using a ZrO_2-CaO oxygen probe.

Atmospheres	Air	Ar-1%O_2	Ar	high purity Ar	Ar-1%H_2
$p(O_2)$ / atm	2.0×10^{-1}	1.3×10^{-2}	7.1×10^{-5}	3.2×10^{-6}	1.6×10^{-10}

The sample powders were placed in the Pt-20mass%Rh crucible and heated up to 1773 K under air. Then the inner cylinder (Pt-20mass%Rh bob) was immersed into the sample melts and we started to turn the inner cylinder to monitor the relative torque. The viscosity of the sample melts could be continuously collected with the melting time. We changed the atmosphere after the viscosity of the samples melts became constant under each of the atmosphere. The

experimental conditions of the viscosity measurements were listed in **Table 3**. The errors of the viscosity measurements were within ±5%.

Table 3 Experimental conditions for the viscosity measurements.

Temperature	1773 K
Atmospheres	Air, Ar-1%O_2, Ar, high purity Ar, Ar-1%H_2
Sample weight	60.0-70.0 g
Immersion depth of inner cylinder	10.0 mm
Revolution speed of inner cylinder	30 rpm

2.3. Oxidation state analysis of iron ions in the samples

The samples, which were synthesized with the same procedure as the samples for the viscosity measurements, were melted in a Pt-20mass%Rh crucible (amount of the sample: 20 g, internal diameter of the crucible: 36 mm) for 270 min. Since the viscosity of the sample melts became constant after 120-150 min melting under Air, Ar and Ar-1%H_2 atmosphere (as described in the following section (Fig.2)), the melting time of 270 min was enough time to equilibrate with the oxygen in the gas phases at 1773 K under each of the atmosphere. After that the samples were quenched on cupper plates. The oxidation states of the iron ions (Fe^{2+} and Fe^{3+}) for these quenched vitreous samples were quantitatively determined by wet chemical analysis; total-Fe and Fe^{2+} content were determined by titration method with ethylenedinitrilo tetraacetic acid (EDTA) and with potassium dichromate, respectively. Fe^{3+} content was calculated by subtracting the Fe^{2+} content from the total-Fe content.

3. Results and Discussion

Figure 2 represents the change in the viscosity of the NSF melt with the melting time at 1773 K as an example. As shown in the Fig.2, the viscosity of the melts decreased with melting time under each of the atmosphere. It should be noted that the viscosity of the NSF melt decreased with melting time even under air. In the previous paper [21], similar phenomena were reported in the CaO-SiO_2-Fe_xO system under air. In that paper, we clarified the phenomena was due to the change in the coordination structure of Fe^{3+} ions. Similarly, the viscosity decrease of the NSF during the melting under air would also be due to an increase of octacoordinated Fe^{3+}, which behave as a network modifier, in the present study. When the atmosphere were changed from air to Ar-1%O_2, the viscosity started to decease with the melting time and the viscosity became constant after 120 min melting under Ar-1%O_2 atmosphere. It indicated that it took around 120 min to achieve the Fe^{2+}-Fe^{3+} equilibration in the melts. Similarly, viscosity decreased with the melting time also under Ar, high purity Ar and Ar-1%H_2 atmospheres. Moreover, the viscosity change with melting time in the LSF and the KSF melts shown same tendency as the NSF melt. We employed the viscosity of the samples, which were melted until the viscosities became constant, as an equilibrated value under each of the atmosphere.
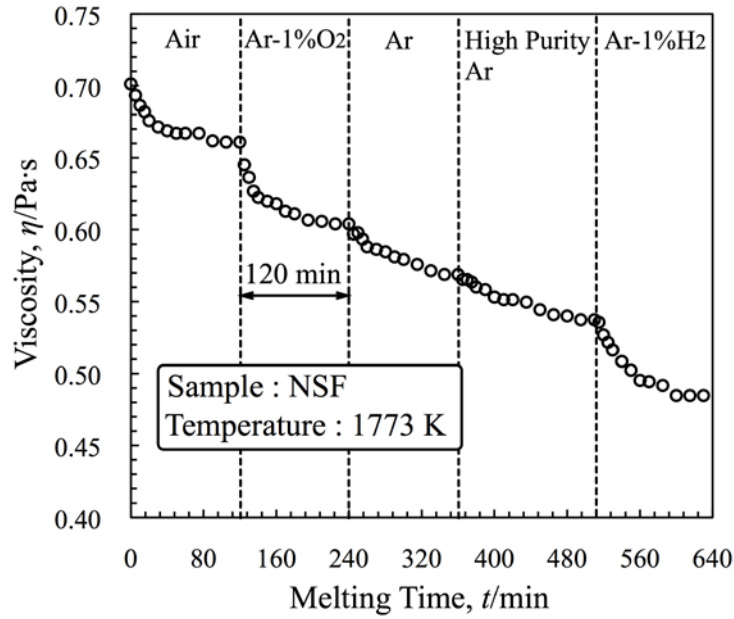
Fig.2 Change in the viscosity of the NSF melts with the melting time at 1773 K. We changed the atmospheres after the viscosity of the melts became constant at each of the oxygen partial pressure.

Generally, Fe^{3+} ions exist as several kinds of complex anions such as FeO^+, $Fe_2O_5^{4-}$, FeO_3^{3-}, FeO_4^{5-} in silicate melts [22]. Morinaga *et al.* [23] reported that Fe^{3+} ions mainly existed as FeO_3^{3-} or FeO_4^{5-} in the $30R_2O$-$60SiO_2$-$10Fe_2O_3$(mol%)(R=Li, Na, K) glasses. When Fe^{3+} ions in the present samples were assumed to exist as the FeO_3^{3-} complex anions, Fe^{2+}-Fe^{3+} redox equation could be expressed as the following equation [22].

$$Fe^{2+}(liq.) + \frac{1}{4}O_2(gas) + \frac{5}{2}O^{2-}(liq.) = FeO_3^{3-}(liq.) \ldots (2)$$
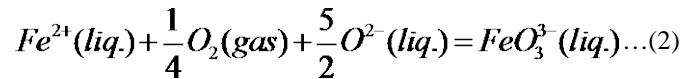
As written in the equation (2) the value of Fe^{3+}/Fe^{2+} depends on the oxygen partial pressure of the gas phase and the activity of O^{2-} ions in the liquid phase, namely basicity. **Figure 3** shows the ratio of Fe^{3+} to Fe^{2+} (Fe^{3+}/Fe^{2+}) in the LSF, NSF and KSF glasses quenched from 1773 K. The value of Fe^{3+}/Fe^{2+} linearly increased with the oxygen partial pressure in all the system. The increase of the Fe^{3+}/Fe^{2+} in the samples indicated that the reaction (2) displaced to the right with an increase in the oxygen partial pressure in the gas phase. As shown in Fig.3, the value of the Fe^{3+}/Fe^{2+} in the samples was in the order of the cationic radius of the alkali cations (K>Na>Li) when the oxygen partial pressure was comparable. It is difficult to directly observe the activity of O^{2-} ions in the melts. However, Duffy and Ingram [24] established the optical basicity, which could quantify the relative electron donor power of the glass system. Namely, the optical basicity is positively correlated with the activity of O^{2-} ions. Duffy [25] calculated the theoretical optical basicity of the $R_2O \cdot 2SiO_2$(R=Li, Na, K) glass, which is the solvent of the present R_2O-SiO_2-Fe_xO system, and the optical basicity has been in the order of $K_2O \cdot 2SiO_2 > Na_2O \cdot 2SiO_2 > Li_2O \cdot 2SiO_2$. The results indicated the activity of O^{2-} ions is the higher in the larger alkali ion containing system. Therefore, the increase of the Fe^{3+}/Fe^{2+} with the cationic radius of alkali cation has been due the reaction (2) displaced to the right with an increase in the activity of O^{2-} ions in the melts.
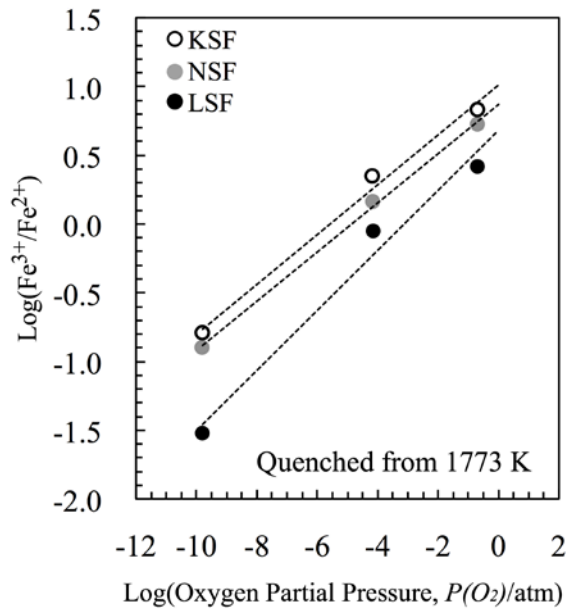
Fig.3 Effect of the oxygen partial pressure, $p(O_2)$, on the ratio of Fe^{3+} to Fe^{2+} in the LSF, NSF and KSF glasses quenched from 1773 K. All samples were melted enough time to equilibrated with the oxygen in the gas phases before quenching with cupper plates.

Figure 4 represents the effect of the ratio of Fe^{2+} to total Fe (Fe^{2+}/total-Fe) on the viscosity (equilibrated value) of the present R_2O-SiO_2-Fe_xO system. The viscosity of the melts decreased with increasing the Fe^{2+}/total-Fe in all the melts. The data indicates that the increase in Fe^{2+} ion that behaves as a network modifier would result in depolymerization of the silicate anions.
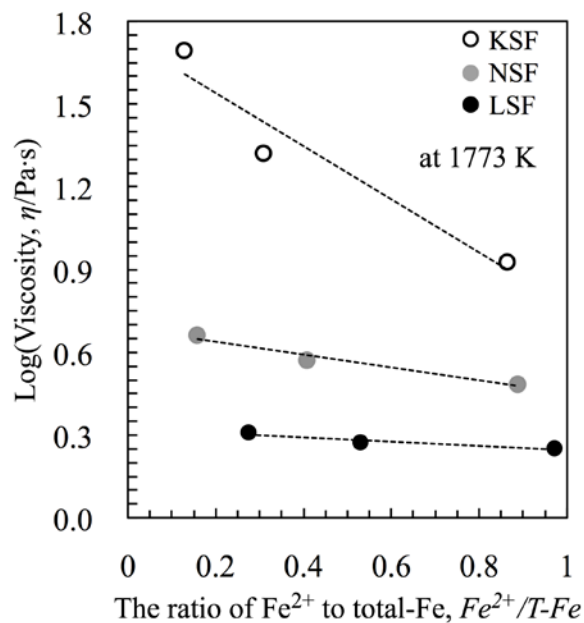

Fig.4 Viscosity variation of the LSF, NSF and KSF melts with the ratio of Fe^{2+} to total Fe ions at 1773 K.
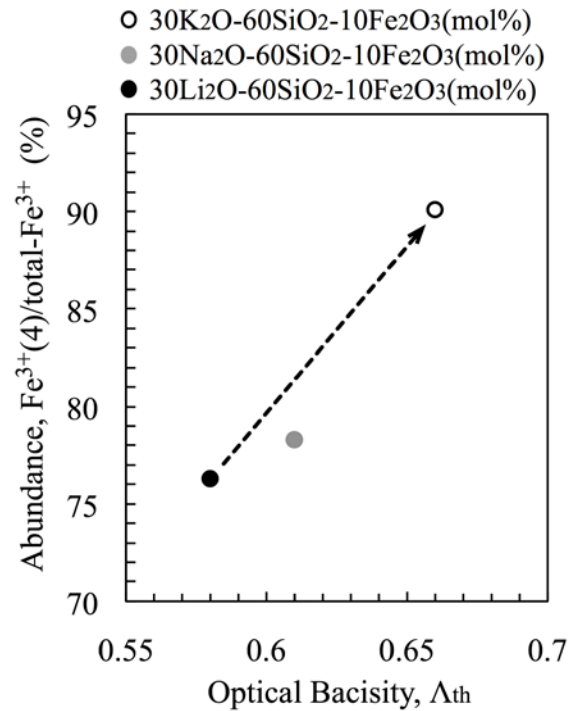
Fig.5 The relationship between the abundance of $Fe^{3+}(4)$ in the $30R_2O$-$60SiO_2$-$10Fe_2O_3$ (mol%) glasses and the theoretical optical basicity of $R_2O \cdot 2SiO_2$ (R=Li, Na, K) glasses. Morinaga $et\ al.$ [23] determined the fractions of $Fe^{3+}(4)$ and $Fe^{3+}(6)$ ions by using Mössbauer spectroscopy. The vertical axis shows the percentage of $Fe^{3+}(4)$ reported in the reference [23]; they reported the rest of the Fe^{3+} ions exist as $Fe^{3+}(6)$. In their study, no Fe^{2+} ions could be detected in the glasses, which were melted 6 hours under air before quenching; the melting temperature of the samples were not described in their paper. The theoretical optical basicity of $R_2O \cdot 2SiO_2$(R=Li, Na, K) glasses, which reported by Duffy[25], was employed as the horizontal axis.

It should be also noted that the viscosity of the melts was in the order of alkali cationic radius (K > Na > Li) when the Fe^{2+}/total-Fe in the melts was comparable (Fig.4). Fe_2O_3 is known as an amphoteric oxide and its behavior is depending on the basicity in the system to which it is added. In the higher basic system, Fe_2O_3 coordinated to four oxygen ions $(Fe^{3+}(4))$ and behaves as a network former, while it coordinated to six oxygen ions $(Fe^{3+}(6))$ and behaves as a network modifier when the basicity of system is the lower. Morinaga $et\ al.$ [23] examined the Fe^{3+} coordination in the $30R_2O$-$60SiO_2$-$10Fe_2O_3$ (mol%) glasses by using Mössbauer spectroscopy. **Figure 5** shows the relationship between the theoretical optical bacisity of the $R_2O \cdot 2SiO_2$(R=Li, Na, K) glasses and the abundance of $Fe^{3+}(4)$ in the $30R_2O$-$60SiO_2$-$10Fe_2O_3$(mol%)(R=Li, Na, K) glasses. As shown in Fig.5, the abundance of $Fe^{3+}(4)$ increased with increasing the optical basicity of the solvent system $(R_2O \cdot 2SiO_2$(R=Li, Na, K)) to which iron oxide was added. Since the abundance of $Fe^{3+}(4)$ is in the order of the alkali cationic radius, the viscosity of the present R_2O-SiO_2-Fe_xO (R=Li, Na, K) melts was the higher in the larger alkali cation containing system. It could be mentioned that the viscosity of iron oxide containing silicate melts is not only dominated by the oxidation state of iron but also affected by the coordination of Fe^{3+} ions. In addition, the basicity of the solvent system plays important role to control the oxidation state of iron ions and the Fe^{3+} coordination.

4. Conclusion

We examined the viscosity change with the oxidation state of iron ions for the R_2O-SiO_2-Fe_xO (R=Li, Na or K) system by rotating cylinder method. The ratio of Fe^{3+} to Fe^{2+} in the R_2O-SiO_2-Fe_xO glasses increased with the oxygen partial pressure in all the samples. It should be also noted that the ratio of Fe^{3+} to Fe^{2+} was in the order of alkali cationic radius (K > Na > Li) when the oxygen partial pressure was comparable.

The viscosity of all the R_2O-SiO_2-Fe_xO melts decreased with increasing the ratio of Fe^{2+} to total-Fe. The data indicates that Fe^{2+} ions behave as a network modifier in the silicate melts. In addition, the viscosity of the melts was in the order of alkali cationic radius (K > Na > Li) when the ratio of Fe^{2+} to total-Fe in the melts was comparable. It was due to the change in the coordination structure of Fe^{3+} in these melts.

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